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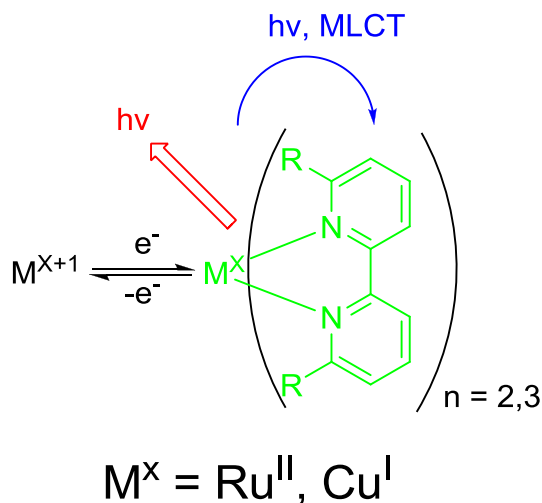
Cu^I versus Ru^{II}: Dye-Sensitised Solar Cells and Beyond

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Graphical abstract:



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Abstract

Ru(II) complexes have long played the central role in photochemical conversion of sunlight leading to dye-sensitised solar cells with high power conversion efficiencies. Cu(I) complexes have been recognised as possessing comparable photophysical and electrochemical properties offering similar function with a cheaper and more abundant metal. DSSCs with significant power conversion efficiency using a Cu(I)-polypyridyl sensitiser have recently emerged and future strategies for further improving performance of these is discussed.

Main text

Fossil fuels are a finite resource and are overwhelmingly believed to lead to climate-altering accumulation of CO₂ in the atmosphere.^[1] In this context, low-cost and efficient conversion of solar energy has emerged as a crucial goal, since solar energy is the only renewable source with the proven capacity to meet the increasing world energy needs.^[2] It has long been known that Ru(II) polypyridyl complexes provide a number of excellent characteristics for the conversion of solar energy including visible metal-to-ligand charge transfer (MLCT) absorption, reversible Ru(II)/Ru(III) redox couple, long-lived excited state lifetime with visible emission, tunable properties through ligand design and stable complexes under appropriate conditions.^[3]

For several decades, much effort has been dedicated to the exploitation of these properties for the conversion of light into usable energy. For example, many studies have explored hydrogen production from water using a multi-component system comprising a Ru-polypyridyl photosensitiser, a sacrificial electron donor, an electron relay and a catalyst for H₂ evolution. As well as comprising separate chemical species these components can be combined into complex assemblies of different functional units^[4] and recently bimetallic Ru(II)-Pt(II) complexes have been shown to lead to photochemical hydrogen production from water using a sacrificial electron donor.^[5] Overall however, conversion of visible light into chemical fuel using molecular photocatalysts without the need for sacrificial reagents remains an elusive challenge. In contrast however, high-efficiency conversion of solar radiation to electrical power, has been achieved using dye-sensitised solar cells (DSSC) based on high-surface-area nanocrystalline TiO₂ films with attached sensitiser dyes that allow efficient light harvesting in the visible spectrum where solar radiation peaks.^[6] The excited-state sensitiser injects an electron into the TiO₂ conduction band. The sensitiser is re-reduced by a solution, or solid-state electrolyte leading to regeneration of the dye in its starting state. The resulting separation of electrons into the TiO₂ conduction band and holes to the electrolyte gives rise to the cell potential. Although classes of sensitiser dye have included organic, phthalocyanine, porphyrin compounds and metal complexes including Os, Pt, Fe and Re,^[7,8] devices with a solar-to-electric power-conversion efficiency of over 10% have been achieved only within the ruthenium-polypyridyl class of dyes such as the commonly used [Ru{4,4'-(CO₂H)-bipy}₂(NCS)₂](N3).^[9]

There has been much discussion in recent years concerning the use of Cu(I) polypyridyls as alternative functional species to the ubiquitous Ru(II) systems.^[10,11,12,13,14] These offer a similar set of key electrochemical, synthetic and photophysical properties (Fig. 1) for application in solar energy conversion as well as other possible technologies including light-emitting diodes,^[15] light-emitting electrochemical cells,^[16] supramolecular architectures and supramolecular machines.^[17] Crucially, Cu(I) polypyridyl complexes differ from other redox-active 1st row transition metal analogues in having a long-lived MLCT excited state that is often emissive. This is due to the filled d¹⁰ subshell of Cu(I) preventing rapid non-radiative decay of the MLCT excited state via metal-centred excited states, which for first-row transition metals are at a similar energy. The low cost and high abundance of Cu compared with Ru leads to an obvious advantage in practical technological applications provided similar functional utility can be achieved.

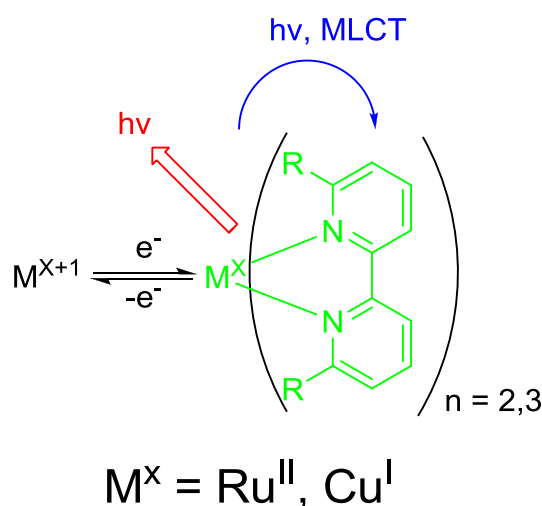


Figure 1. Summary of key properties of Ru(II) ($n = 3$, $R = \text{e.g. H}$) and Cu(I) ($n = 2$, $R = \text{bulky group}$) polypyridyl complexes including bipyridines (as shown), phenanthrolines and mixed-ligand complexes.

An important feature of Cu(I) complexes concerns the expected flattening of the approximately tetrahedral geometry when oxidised or in the MLCT excited state (where the metal is effectively oxidised and the ligand reduced). This necessitates some steric constrain in functionally-useful Cu(I) systems, via for example 2,9-substitution on bipyridyl ligands (Fig. 1), to prevent geometric changes that can slow electron transfer processes and facilitate rapid, non-radiative decay of the MLCT excited state. We can note that the use of such geometric constraint to enable reversible Cu(I)/Cu(II) electrochemistry has parallels with the entatic state of blue copper protein active sites.^[18]

Initial attempts to use geometrically-constrained Cu(I)-based dyes as the sensitiser in nanocrystalline DSSCs (Fig. 2(a),(b)) led to low efficiency devices.^[19,20] With hindsight however, these can be rationalised. Sensitiser

dyes require to be strongly anchored to the semiconducting oxide and also require appropriate electronic communication between the dye and the nanocrystalline material. These requirements are both normally achieved through carboxylic acid groups and studies of Ru(II)-polypyridyl sensitisers have generally shown the 4,4'-positions on the bipyridyl ligand to be most favourable location for these groups.^[8] This can offer an explanation for the poor performance in the initial studies of Cu(I) complexes as both examples (Fig 2(a), (b)) have the acid functional groups in other positions. In recent months however, Bessho *et al* have reported the first examples of Cu(I)-bipyridyl complexes as dyes for nanocrystalline DSSCs with the anchoring groups located in the 4,4'-positions of the bipyridyl.^[21] This study has now led to solar-to-electric, power-conversion efficiencies of 1.9% (Fig. 2(c)) and 2.3% (Fig 2(d)), with the latter enhancement attributed to better light-harvesting by the more conjugated dye (Fig. 2(d)).

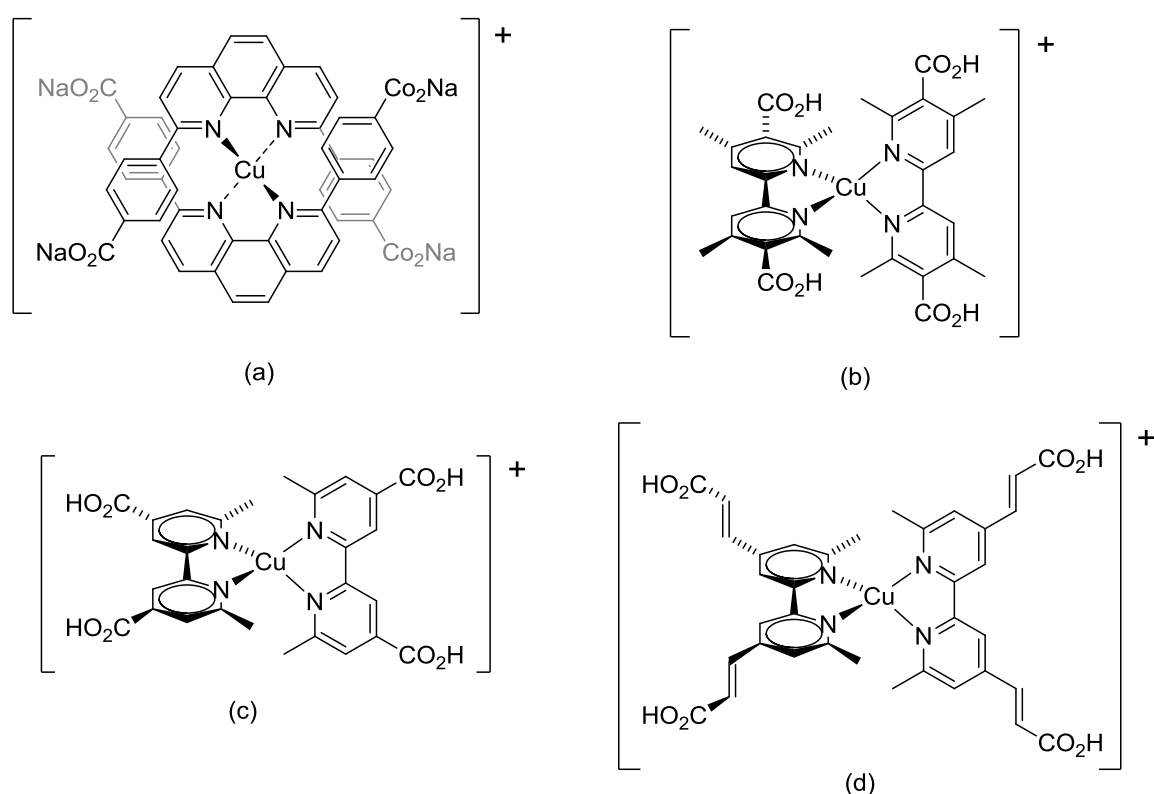


Figure 2. Cu(I) complexes studies as dyes in DSSC

Although the efficiencies achieved using these complexes remain around four times lower than those using the best Ru(II) dyes, the greater abundance of Cu offers considerable opportunity for reduction in cost. Furthermore, the Cu(I) approach has yet to undergo the barrage of investigation and optimisation that has been applied to Ru(II) sensitisers and it can be envisaged that great improvements are yet to come now that the possibility of significant efficiencies has been demonstrated. There are several straightforward design

strategies that can now be used to follow up these results. For example, all the sensitiser shown in Fig. 2 are symmetrical with two identical ligands however asymmetry in the sensitiser can lead to directionality in the light-harvesting transition giving more favourable charge-transfer kinetics in the DSSC device. Asymmetric Cu(I) complexes have yet to be explored in DSSC although interesting examples with high emission quantum yield have been demonstrated in, for example, light-emitting electrochemical cells.^[16] Also in the case of Ru(II) complexes, the highest-efficiency sensitiser are generally neutral or anionic however the Cu(I) examples to date are cationic. The charge on the sensitiser may play a role in determining crucial electron-transfer kinetics in the device and neutral Cu(I) complexes could be readily prepared using an anionic ligand in place of one of the bipyridyl ligands. Furthermore, the recent study by Bessho *et al* emphasised the importance of extending light-harvesting by Cu(I) sensitiser to longer wavelength to better utilise the solar spectrum. They also showed enhanced light harvesting through extended conjugation within the bipyridyl ligand. Cu(I) polypyridyl complexes in general have lower molar absorption coefficients than Ru(II) analogues and strategies to increase light harvesting offer much scope for the enhancement of efficiencies.

With attention to such criteria in the coming years, we can anticipate further jumps in efficiency of DSSCs with sensitiser based on Cu(I). This exciting possibility can only add to the prospect of Cu(I) challenging the long-dominant position of Ru(II) not only in DSSC, but across several fields of photophysical, photochemical and supramolecular applications.

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